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"LOW PRESSURE VAPOR GROWTH OF DIAMOND"

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ABSTRACT

It has been established in several laboratories that diamond can be grown by epitaxy on diamond seed crystals from methane at subatmospheric pressures. The growth rates obtainable at the present time are, however, too slow to be of practical interest. During the second year of this contract we continued to explore means of increasing diamond growth rates at low pressure.

Work was performed in four major areas:

1) continuation of kinetic studies on the direct uncatalyzed growth of diamond from methane and methane-hydrogen gas mixtures,

2) extensive survey of metal catalyzed vapor-liquid-solid (V-L-S) growth experiments using molten transition metals as catalysts,

3) initiation of experiments on the growth of diamond seed crystals using free radicals as a source of carbon, and

4) the growth of boron doped, P-type, semiconducting diamond from the vapor.

The kinetic studies on the uncatalyzed growth indicate the growth rate is slightly less than first order in methane partial pressure and that the activation energy is 55 ± 5 Kcal/gmole. The addition of hydrogen to the reaction mixture decreases the growth rate but also suppresses the formation of graphite. Maximum initial growth rates of 13%/hour on 0-1 μ nominal size diamond powder have been observed. This corresponds to an average linear growth rate of only 7×10^{-2} μ/day. However, extrapolations to higher temperatures, inaccessible in our present apparatus, indicate that this method holds promise as a means for upgrading fine diamond powder into larger, useful grades.

An extensive survey of V-L-S methods showed no evidence of diamond growth. Literature reports of the growth of diamond whiskers by V-L-S could not be confirmed. The newly initiated work on growth of diamond via free radicals has not progressed to the point where any definitive results have been obtained.

The growth of boron doped P-type semiconducting diamond from the vapor was successfully demonstrated. These results provided further confirmation of metastable diamond growth and also substantiate the role of boron as the electrically active impurity center in semiconducting diamond. The boron also performs a catalytic function during the growth process.

The research is being performed in the Engineering School of Case Western Reserve University under the direction of Professors John C. Angus and Nelson C. Gardner. One post-doctoral research fellow and three graduate students are associated with the project.

I. PURPOSE OF THE RESEARCH

The purpose of the research is to achieve rapid growth of high quality diamond from the vapor at low pressures.

II. RELEVANCE OF THE RESEARCH

Vapor growth of diamond eliminates the necessity of super high pressure conditions and holds the promise of providing high quality diamond at low cost as well as in crystalline forms previously unattainable: for example, filaments and thin films.

The application of low pressure diamond growth closest to practical realization is the upgrading of very fine diamond abrasive powders into size ranges of commercial importance; e.g., converting 1 μ powder into 20 μ powder.

III. PREVIOUS WORK

Early workers discussing the possibility of low pressure diamond growth were Professor Bridgman [1], Dr. Guy Suits [2], Professor A. R. Ubbelohde [3] and Dr. J. J. Lander [4]. Early work by Eversole [5], experiments in our laboratory [6] and at the Physical Chemistry Institute in Moscow [7], have established that diamonds can be grown at low pressures. All of the processes (proposed or reduced to practice) involve the homoepitaxy of carbon on a diamond substrate. For example, in the work of Eversole [5] and Angus [6], simple gaseous hydrocarbons are thermally decomposed in the presence of diamond seed crystals.

Deryagin [7], on the other hand, in some of his work uses a version of the vapor-liquid-solid (V-L-S) technique that has been successfully employed for growing silicon crystals [8]. Deryagin's work is interesting in that he

reports the growth of diamond whiskers using molten Fe, Ni, Cc and Mn as the V-L-S agents. He also has recently reported the growth of spherical diamonds by the same process. Deryagin and co-workers at the Institute for Super Hard Materials in Kiev are also starting a pilot plant for a commercial low pressure process using the direct, uncatalyzed, deposition of carbon onto diamond seed from methane [9].

Several other processes for the low pressure growth of diamond have been briefly reported. A patent by Courvoisier [10] describes an electrolytic approach. Nelson et al. reported the growth of "white carbon" at extremely high temperatures from the vapor [11]. Aisenberg and Chabot have recently reported on the growth of diamond-like films by ion beam deposition [11,12,13].

There is also evidence that carbon in the outer atmospheres of stars may be present as diamond particles rather than graphite [15]. This striking possibility indicates that nucleation and growth processes for the metastable formation of diamond may be more easily and widely achieved in nature than previously imagined. It also indicates that the relative growth rate of diamond from the vapor compared to graphite may be quite large. The data of L. Brewer [16] on the accommodation coefficient of carbon atoms on graphite tends to support this position. Professor Brewer's comments were made a part of Reference [15].

Our group has for the past several years been making a systematic exploration of growth parameters (temperature, pressure, gas phase composition, impurity levels, and supersaturation) and how they affect growth. Substantial progress has been made including: (1) increase in growth rates of approximately one order of magnitude, (2) attainment of diamond yields of virtually 100% (no graphite), (3) accurate, in situ, rate measurements as a function of

temperature and gas phase composition in an ultra high vacuum microbalance, and (4) growth of boron doped, P-type semiconducting diamond from methane-diborane gas mixtures.

IV. RESULTS DURING PAST CONTRACT PERIOD

A. Uncatalyzed Growth of Diamond from Methane and Methane/Hydrogen Mixtures

A continuing series of kinetic studies on the direct, uncatalyzed growth of diamond from methane and methane/hydrogen mixtures was made. These runs were made in the ultra high vacuum microbalance system described in our previous report [17].

Typical results of growth runs are shown in Figures 1 through 3. Note that the growth rate during a run decreases as growth proceeds. The maximum initial growth rate observed on 0 to 1 μ nominal size natural diamond seeds was 13% per hour at a temperature of 1165°C and a methane pressure of .41 Torr. After a period of growth, the original growth rate may be partially recovered by cleaning in H_2 at *circa* 50 atm and 1040°C. The initial growth rate on virgin diamond powder is about 25% higher than the initial rate observed during the second run on the same sample. On the third and subsequent runs on the same sample the initial rate decreases only about 2 to 3% each run. This latter effect may simply be caused by a decrease in the gross, superficial surface area. The growth rate, $\frac{1}{M}\frac{dM}{dt}$, for a surface area limited process is inversely proportional to the average particle radius (See Equation 3, Section V-B of this report.). The large decrease in rate from the first run to the second may involve the using up of active sites on the surface which are not regenerated by the hydrogen cleaning process.
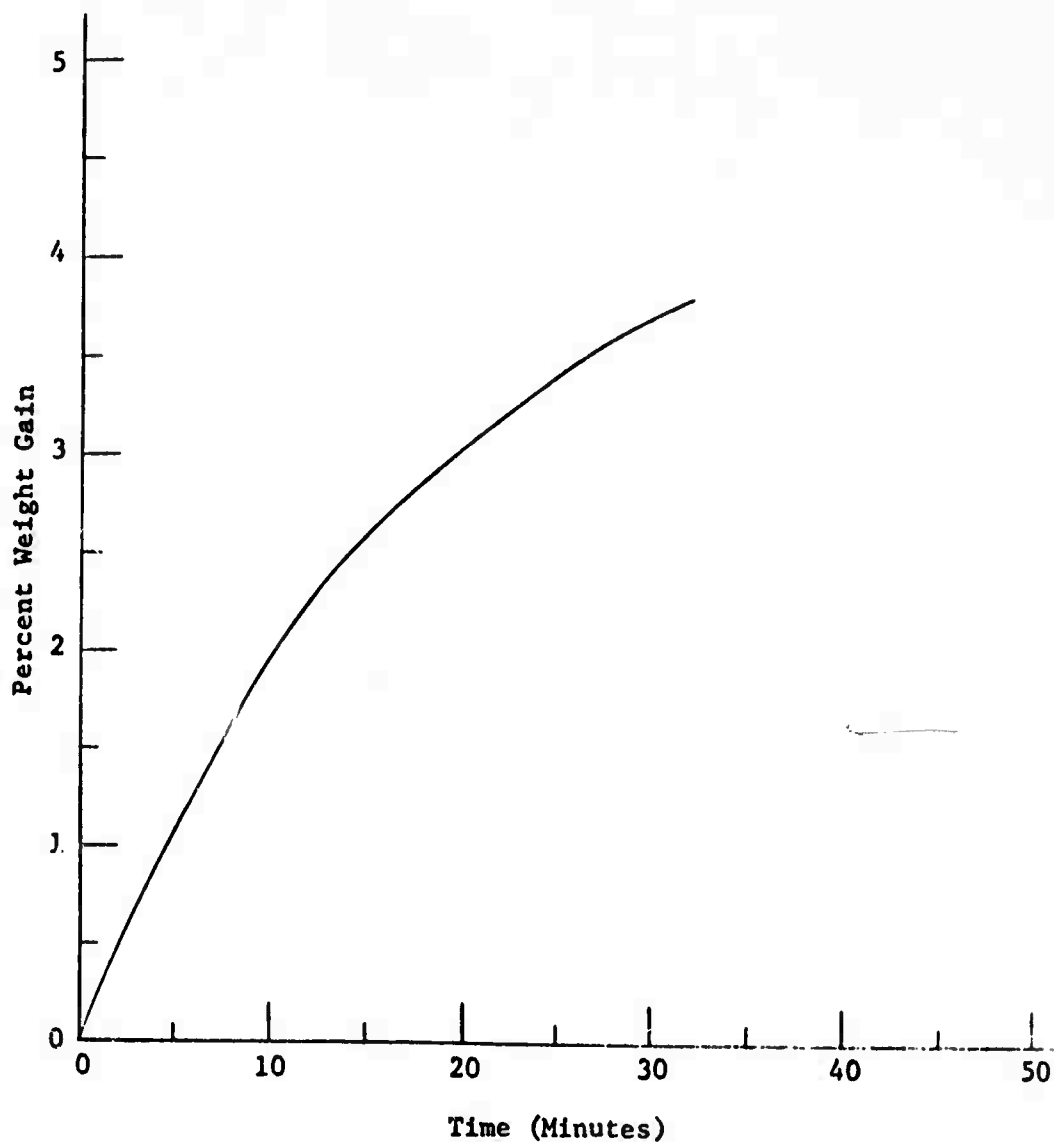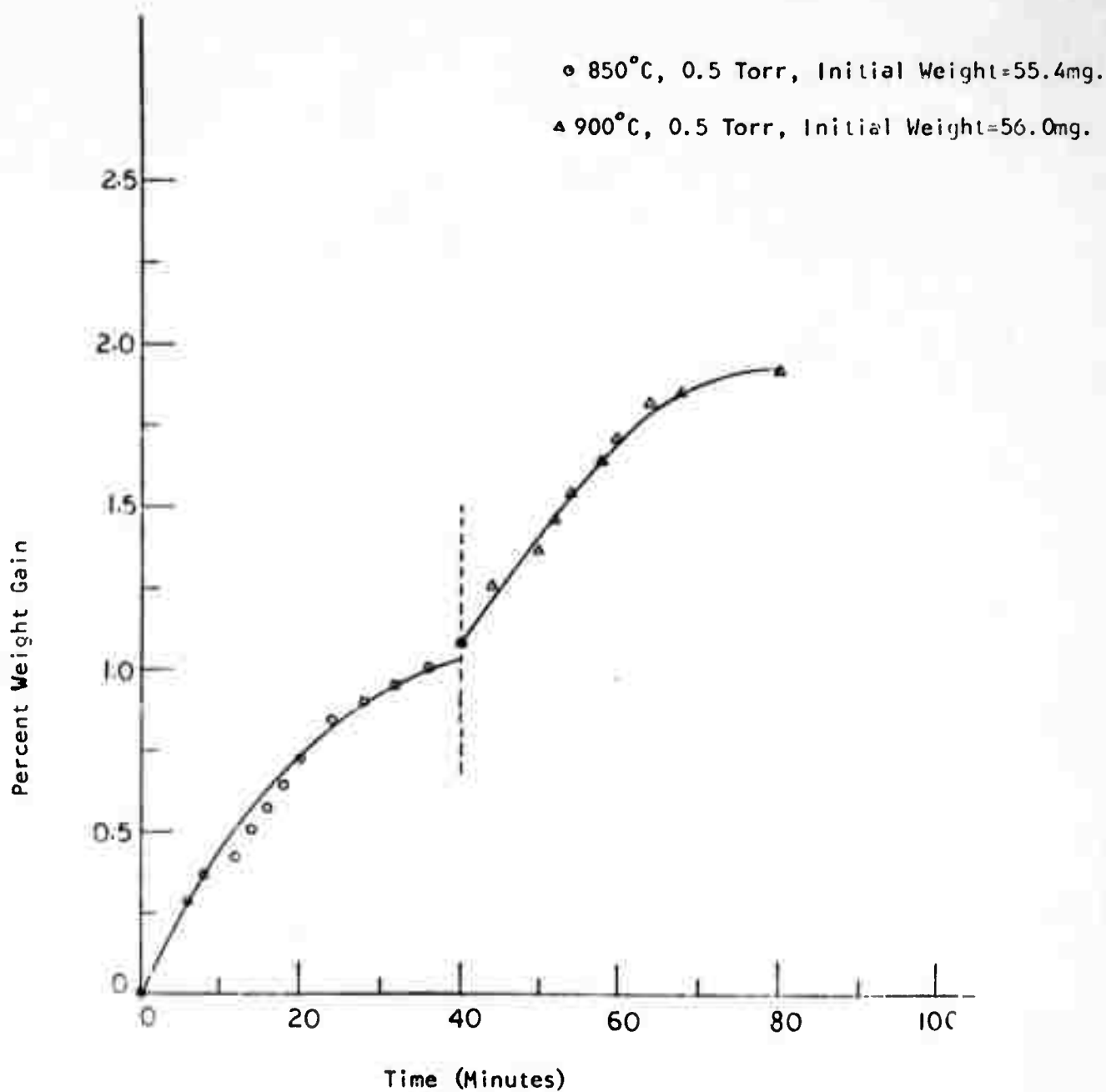
Percent weight gain [based on initial weight = 49.752 mg.] of diamond (O-1 mic.) as a function of time for Run 24, using methane-hydrogen gas mixture at 0.61 Torr [methane partial pressure = 0.414 Torr; hydrogen partial pressure = 0.196 Torr] and 1165°C.

Figure 1

4
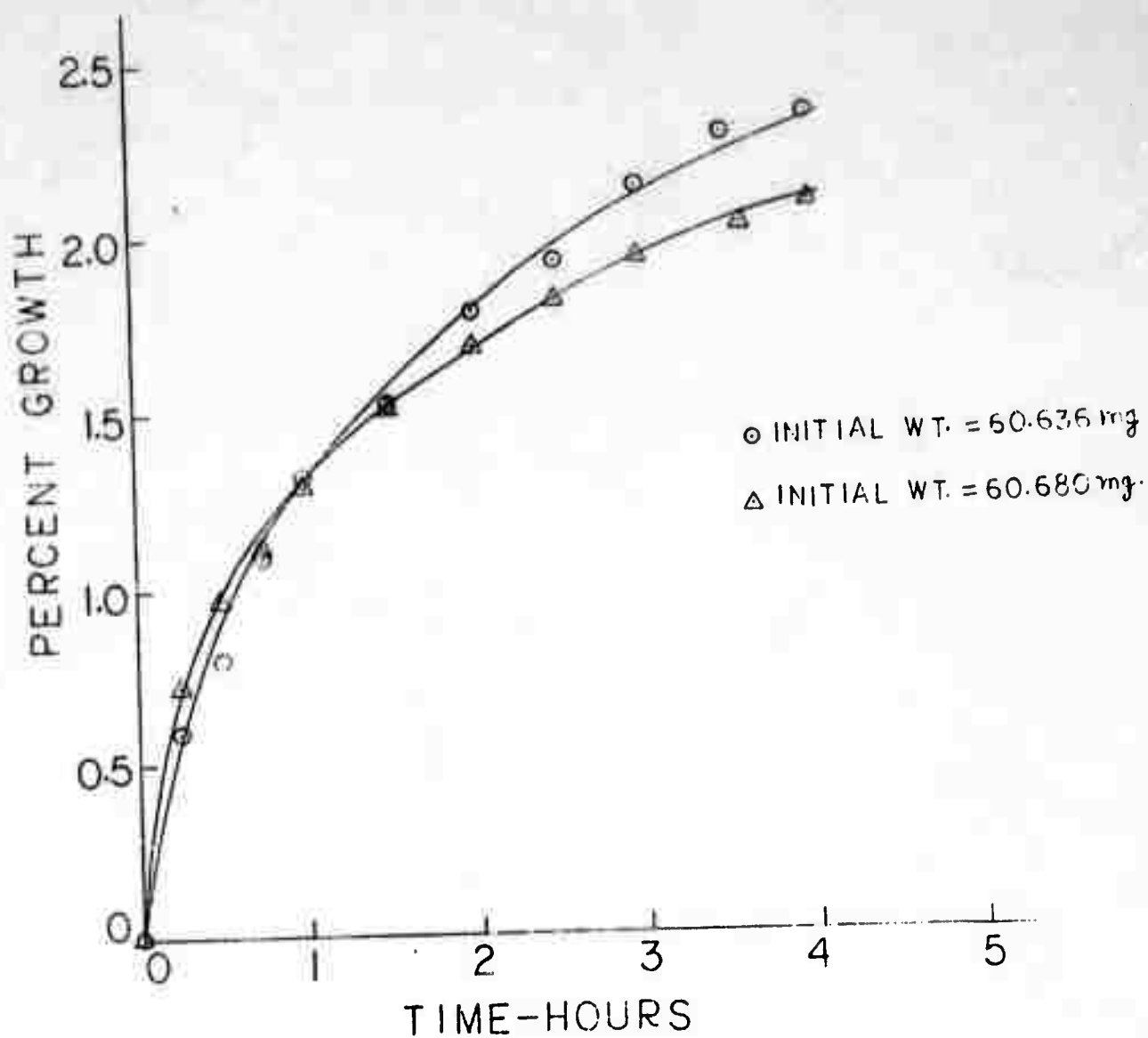
Percent growth of diamond powder (0-1micron) as a function of time, at 1×10^2 Torr and 950°C, for two experiments using methane.

Figure 2

5

○ 850°C, 0.5 Torr, Initial Weight=55.4mg.
▲ 900°C, 0.5 Torr, Initial Weight=56.0mg.

Percent Weight Gains (Based On Initial Weights) Of Diamond
(0-1 mic.) As A Function Of Time For Two Different Temperatures
Using 80% Methane And 20% Hydrogen Gas Mixture.

Figure 3

There are several possible reasons for the continual decreasing rate of growth during a run. The first carbon atoms may fill in defect sites such as steps, kinks, etc. The surface becomes atomically smoother and therefore subsequent nucleation and growth processes become more difficult. Another possible explanation is slow contamination of the surface by some impurity such as silicon. A third possibility is decreased rates of mass transfer as the diamond particles sinter together. A fourth is contamination by graphite.

The growth rate appears to be slightly less than first order in methane partial pressure. See Figures 4, 5 and 6. The addition of hydrogen to the gas phase decreases the growth rate (see Figure 7); however, it has the beneficial effect of suppressing the formation of graphite. Estimates of the activation energy of the growth process were made by applying a step jump in temperature, while continuing to monitor the growth rate. These measurements give an activation energy of 55 ± 5 Kcal/gmole. See Figures 8 and 9. Our value of the activation energy can be compared with the value of 80 Kcal/gmole reported by Deryagin [9].

Our results indicate that the best conditions for low pressure diamond growth may be at higher temperature and methane partial pressures than previously employed by us, Eversole, or Deryagin. In order to keep graphite from forming at these conditions, it is necessary to operate with substantial partial pressures of hydrogen. In addition, it is crucial to exclude all traces of oxygen, which serves as a catalyst for graphite formation. Experiments designed to determine the optimum conditions are continuing. At the present time it appears that one should operate at the highest possible temperature, i.e., just below the point where the spontaneous graphitization of the diamond substrate takes place at an appreciable rate. This may be as high as 1800°C, well above
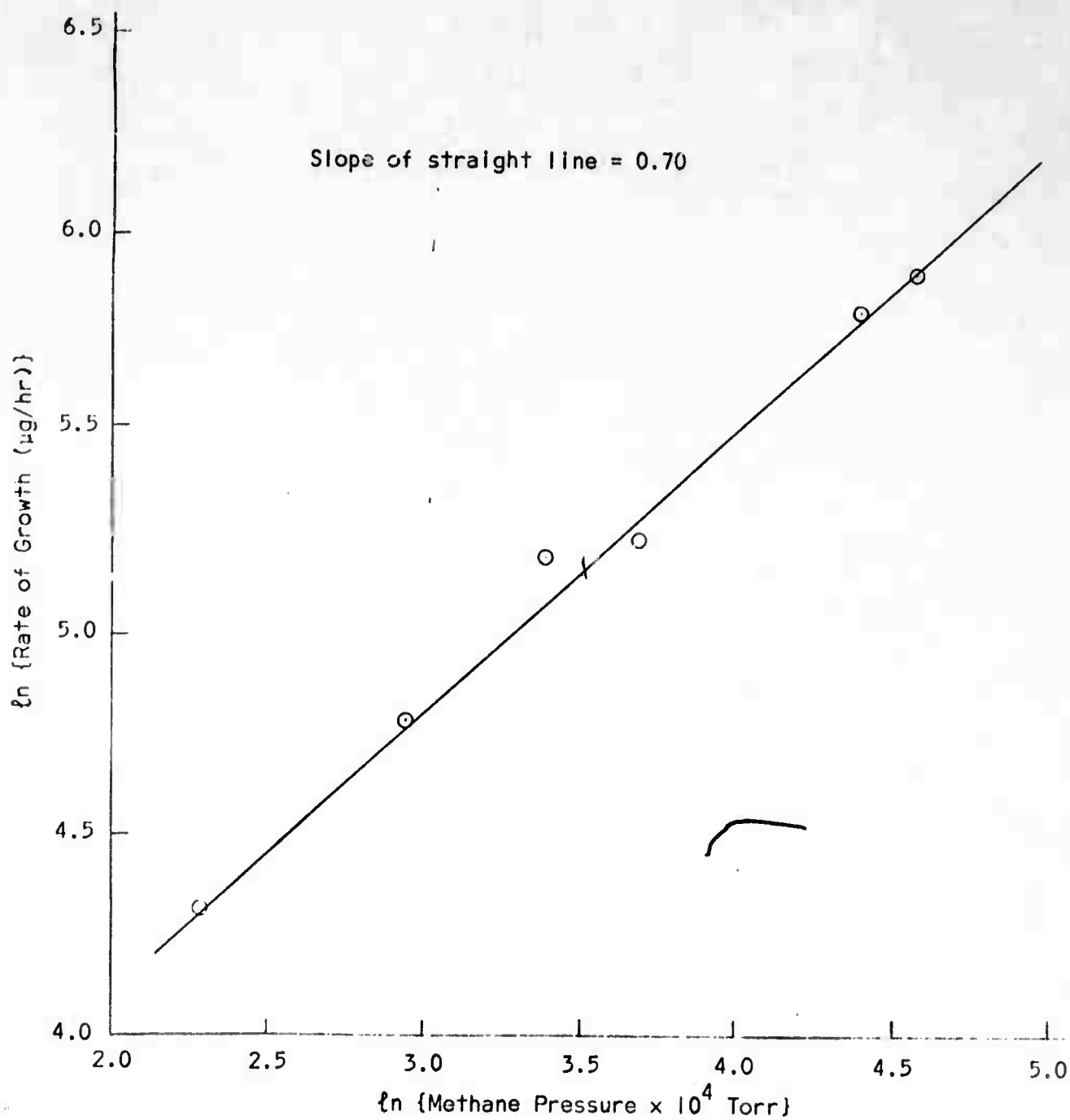
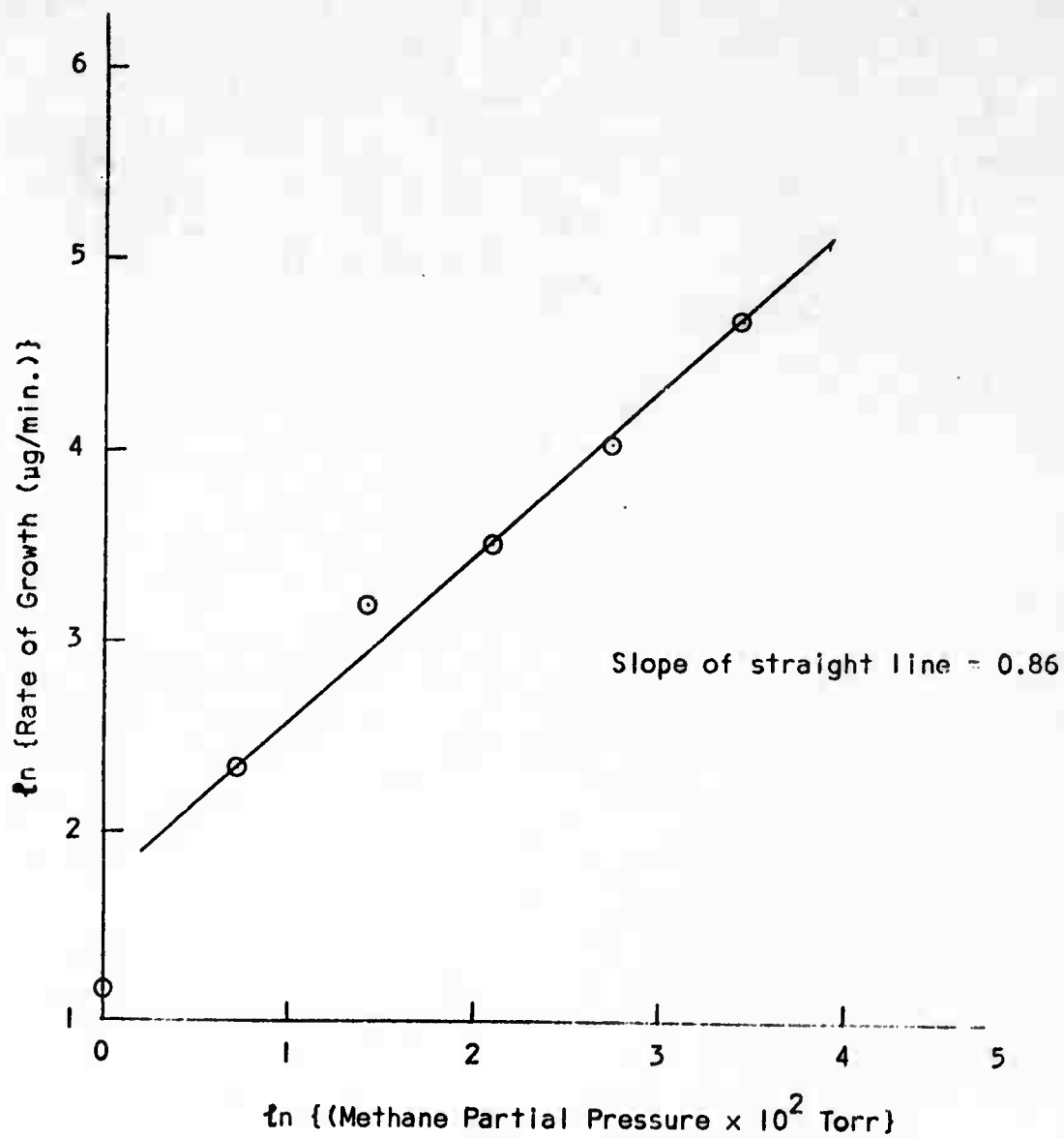DIAMOND (0-1 μ) GROWTH RATE AS A FUNCTION OF METHANE PRESSURE
AT 1104.7°C.   WEIGHT OF SAMPLE = 60 mg.

Figure 4

8
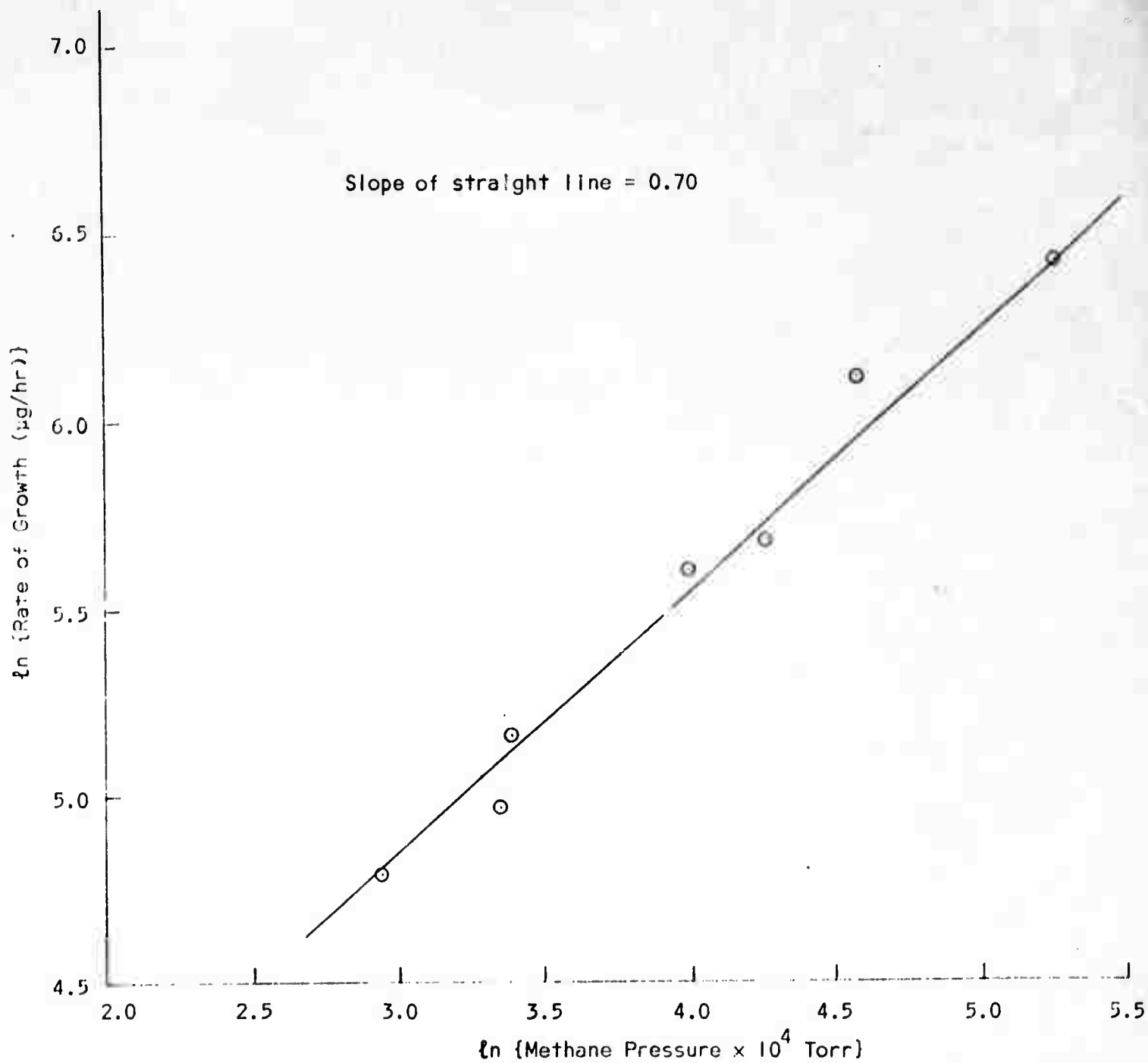
DIAMOND (O-1μ) GROWTH RATE AS A FUNCTION OF METHANE PRESSURE AT 1128.7°C.
WEIGHT OF SAMPLE = 60 mg.

Figure 5

9

GROWTH RATE OF DIAMOND (0-1μ) AS A FUNCTION OF
METHANE PARTIAL PRESSURE AT A HYDROGEN PARTIAL PRESSURE
OF 0.45 TORR AND AT 1165.0°C.   SAMPLE WEIGHT = 60 mg.

Figure 6

10
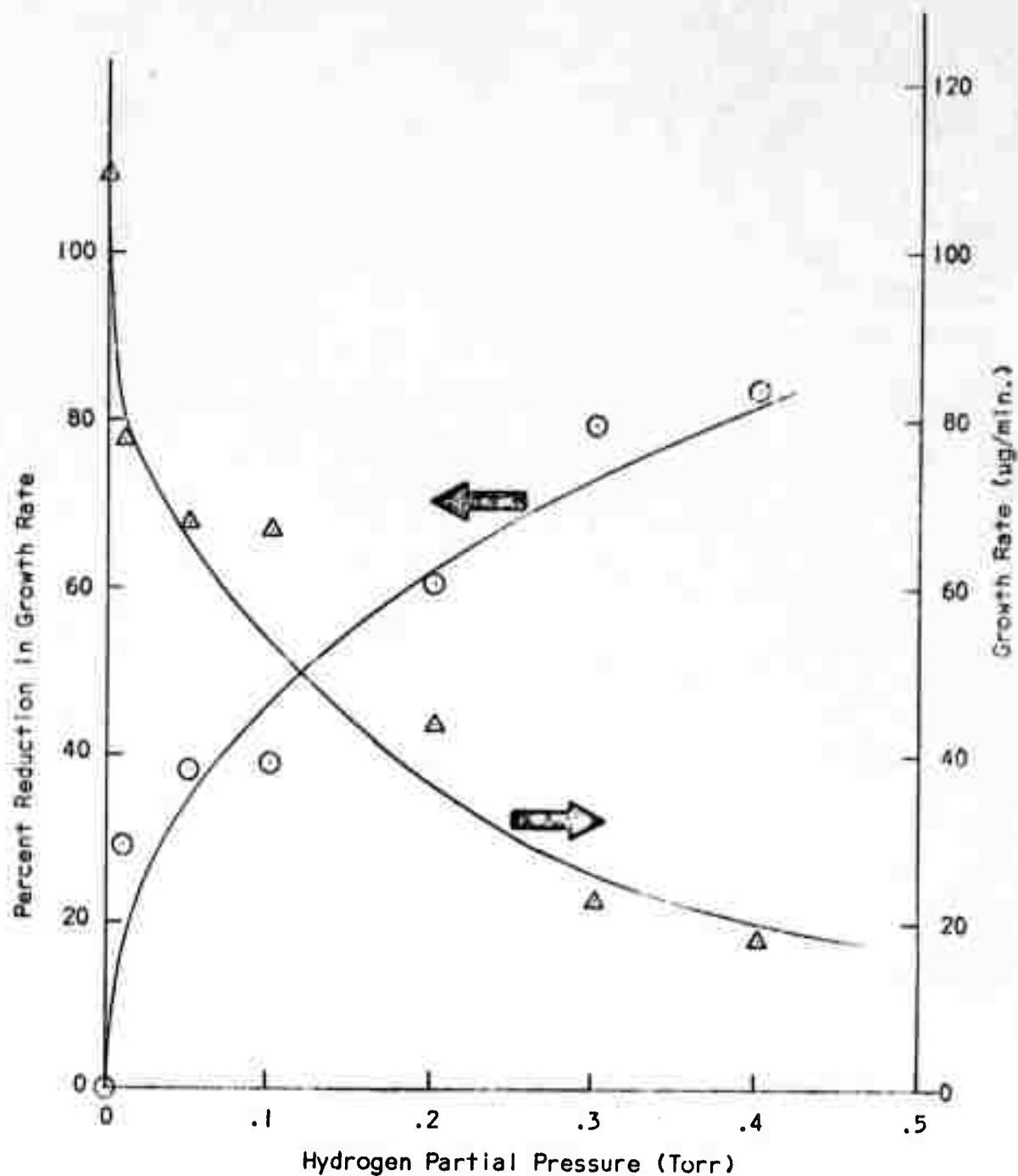
PERCENT REDUCTION OF GROWTH RATE (AS COMPARED TO PURE METHANE
GROWTH RATE) OF DIAMOND (0-1 μ) AND ABSOLUTE GROWTH RATE
(WEIGHT OF SAMPLE = 60 mg.) AS A FUNCTION OF HYDROGEN
PARTIAL PRESSURE AT A METHANE PRESSURE OF
0.1 TORR AND 1170.0°C.

Figure 7

11
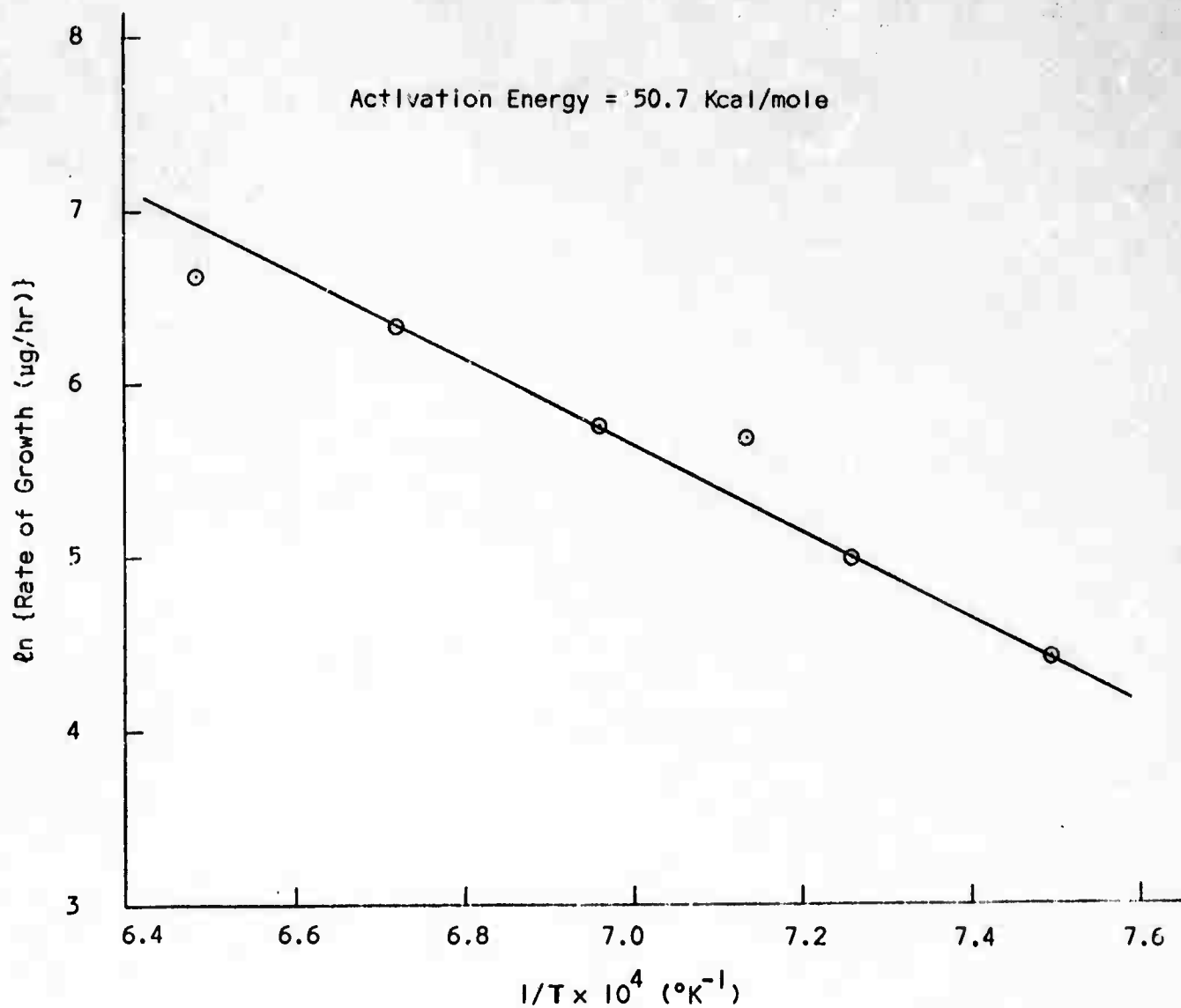
DIAMOND (0-1 μ)GROWTH RATE DEPENDENCE ON TEMPERATURE AT A
METHANE PRESSURE OF 3.0x10^{-3} TORR.   WEIGHT OF SAMPLE = 60 mg.

Figure 8

12
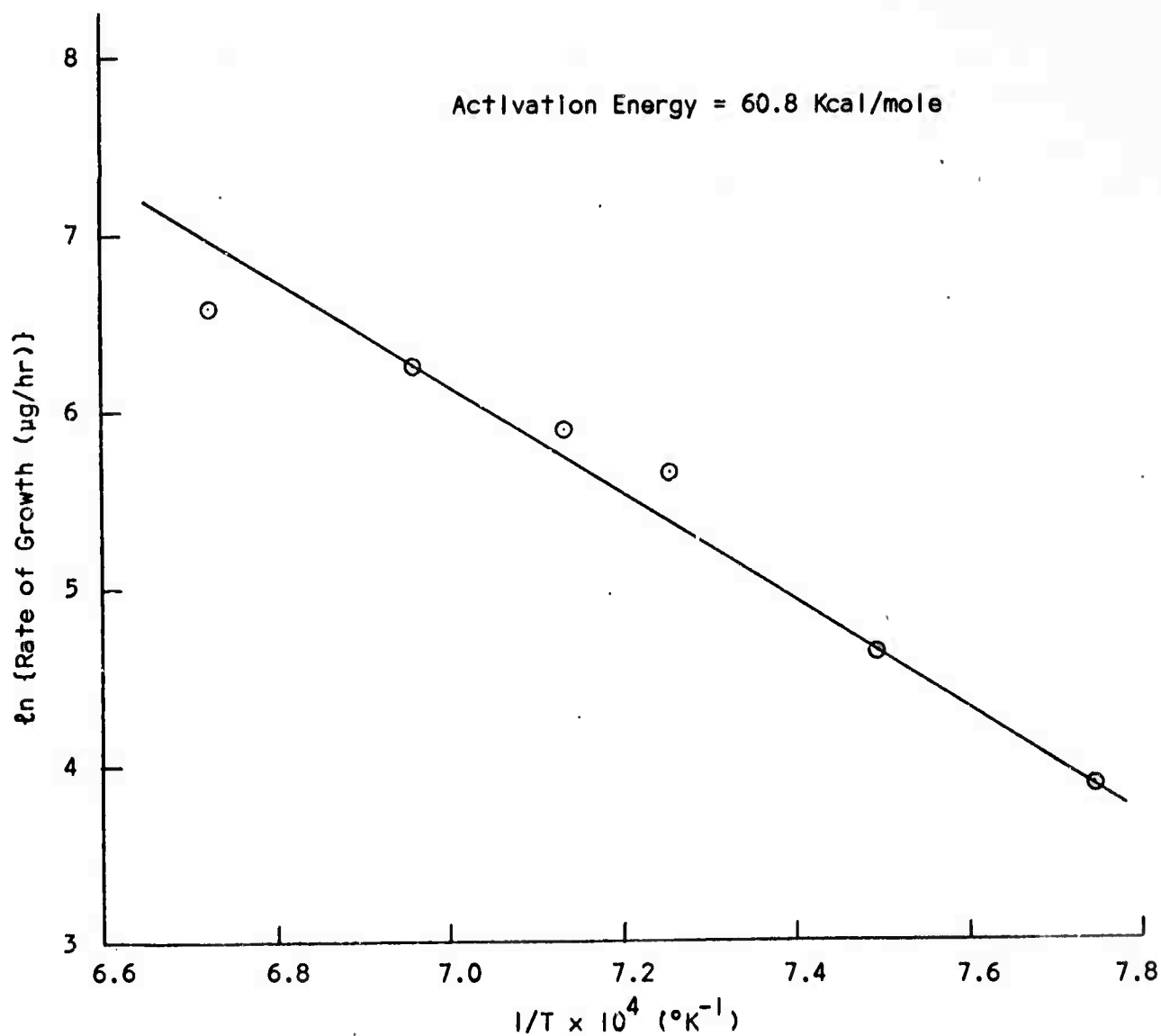
DIAMOND (0-1 μ) GROWTH RATE DEPENDENCE ON TEMPERATURE AT A
METHANE PRESSURE OF 5.0x10⁻³ TORR.   WEIGHT OF SAMPLE = 60 mg.

Figure 9

13

the upper limit of our present apparatus.

Another very interesting facet of this work is the observation of sintering of the diamond powders into a compact structure. This sintering is observed not only when growth of new diamond takes place, but also when the powders are simply annealed in the presence of atomic hydrogen.

B. Metal Catalyzed Growth of Diamond at Low Pressures

During the past contract period we have done very extensive work on the V-L-S method similar to the work of Deryagin [7]. In this process a thin layer of transition metal is placed on the diamond surface before deposition of carbon takes place. The diamond growth occurs at the metal diamond interface.

For metals we have employed Fe, Ni, Co and Fe-Ni alloys. Temperatures ranged from just below the appropriate eutectic temperature to approximately 200°C above the eutectic temperature. In most cases the metal was vapor deposited in situ. Metal thicknesses ranged from 10 Å to 100 Å. In some experiments .005" thick Fe and Ni foil were used. The source of carbon was pure CH_4 at pressures ranging from $< 10^{-3}$ Torr to 20 Torr. The experiments were performed in an ultra high vacuum system described in an earlier report [17].

Numerous features were observed. The most common was a bumpy, hillocky structure, easily observed by optical or low power scanning electron microscopy. The bumps were raised above the original diamond surface. After etching in HNO_3/H_2SO_4, the bumps disappeared and were replaced by pits, each pit corresponding to a previous bump. X-ray identification of the bumps revealed them to be a mixture of metal and graphite. Apparently the metal layer acts as a catalyst for the conversion of the diamond substrate to graphite. The raised bumps are caused by the fact that the density of the newly formed

graphite is less than that of diamond.

In order to lessen the chance of excessive carbon supersaturations which might cause graphite nucleation, we performed several solid-liquid-solid (S-L-S) runs in which a diamond-transition metal-diamond sandwich was employed. The diamonds were small macles with flat (111) faces. The upper diamond was heated with a 11.6 μ beam from a CO_2 laser. The heat flux down through the sandwich maintained a temperature difference of 4°C across the .005" metal foil. Hopefully carbon would dissolve at the upper diamond and diffuse across the metal layer and grow new diamond on the lower, cooler diamond. The maximum carbon supersaturation of only 4°C was well below the supersaturations required for graphite nucleation according to classical nucleation theory. The atmosphere in the chamber was pure CO_2 at 5×10^{-5} Torr No evidence for diamond growth was found in any of these runs.

In some runs a type of temperature gradient zone melting was observed. A molten iron drop on a diamond macle surface was heated obliquely with a laser. The drop would dissolve diamond at the leading (hot) side and precipitate graphite at the trailing (cool) side. The drop would move slowly across the diamond surface toward the laser.

Another interesting observation was the reverse V-L-S process. In this situation a droplet of iron was placed on the (111) plane of a diamond macle and annealed under H_2 at temperatures above the Fe-C eutectic temperature. Diamond dissolved in the molten iron, diffused across to the metal surface where it presumably reacted with the H_2 to form hydrocarbon gases. The metal droplet sank down through the diamond. The net result of the process was a neat, steep sided hole.

It is important to note a unique problem in attempting to grow a metastable crystal by a V-L-S process. Suppose a nucleus of the stable phase (in this case graphite) nucleates in the liquid phase. Because it is the stable phase it has a lower thermodynamic chemical potential than the substrate. The substrate will therefore dissolve and material will be transported down the chemical potential gradient to the stable nucleus.

In our situation the diamond will dissolve and the carbon diffuse to the graphite. On the other hand, if spontaneous nucleation of graphite can be avoided in the liquid phase, the diamond may grow. Our theoretical calculations of the nucleation rate of graphite from liquid iron indicate that supersaturations large enough to grow diamond are entirely feasible without graphite nucleation.

Some extraneous uncontrolled factor, e.g., small amounts of residual oxygen contamination or temperature fluctuations may be promoting the graphite nucleation. Our results with the VLS process are somewhat surprising in view of Deryagin's claims.

Personal conversations with Deryagin indicate that our experimental procedures may be more careful than theirs, especially in the matter of control over impurities and identification of the deposits. At the present time we have also been unable to confirm Deryagin's reports of either diamond whiskers or spherical shaped diamonds. We have observed similar shaped features, but they were not diamond. We have, however, observed other types of hillocky growth features in some VLS runs which we believe may be diamond. These growth features are not, however, found in all runs and require much further study.

C. Growth of Diamond Using Free Radicals

Another area which has received attention by our group is the use of highly reactive gas phase species, e.g., free radicals, as a source of carbon atoms for the diamond epitaxy. The highly reactive free radical, e.g., methyl

should be able to attach itself to the diamond crystal at any surface lattice site irrespective of the presence of a defect. In a sense, the gas phase species carries its own active site with it. We are conducting experiments using dimethyl mercury as the carbon source.

In these experiments a molecular beam of dimethyl mercury is allowed to impinge on the (111) surface of a heated diamond macle. The macle is supported by a thin platinum strip which is resistance heated. Macle temperatures range from 500 to 1000°C, dimethyl mercury pressures from 5×10^{-4} to 1×10^{-2} Torr. In some runs rod and ball shaped surface features were observed. They were soluble in 48% HF solution and are therefore presumably not diamond. A dark film, soluble in HNO_3/H_2SO_4 solution, has also been observed. It is almost certainly graphite, although no further identification was done.

No general conclusions can yet be drawn from these initial experiments. A great deal of exploration of other possible experimental regimes remain to be done.

D. Growth of Boron Doped Diamond from Methane-Diborane Gas Mixtures

A copy of a paper presented at the International Conference on Synthetic Diamond, Kiev, USSR is attached to this report as an appendix.

V. THEORETICAL CONSIDERATIONS

A. Suppression of Graphite Formation

In order to achieve diamond growth it is necessary to suppress both the spontaneous nucleation of graphite carbon from the hydrocarbon gas phase and the spontaneous transformation of the diamond substrate to graphite. The conditions we believe to be necessary to achieve this have been discussed in an earlier report [17]. Briefly, they are: (1) maintain temperature below the temperature at which diamond graphitizes (maximum temperature probably no greater than 1800°C); (2) maintain surface diamond atoms in sp^3 tetrahedral position by presence of an adsorbed layer, e.g., hydrogen; (3) presence of some surface defects to act as nucleation sites; and (4) rigorous exclusion of oxygen and water vapor from system.

The ability of adsorbed hydrogen to suppress the rate of graphitization of diamond has also been observed by others [18]. The catalytic action of oxygen on the graphitization of diamond is a well-known phenomenon observed by many workers.

The role of surface defects, e.g., screw dislocations, steps, kinks, etc., and the crystallographic orientation also play an obviously important role in the vapor growth process. The diamond powders we use for seed crystals present different crystal faces and many types of defects to the supersaturated gas phase. There is presumably a disproportionate number of (111) planes present because that is the natural cleavage plane of diamond. In our experiments we can influence the atomic nature of the surface primarily by the gas molecules that are adsorbed on the surface. The presence of adsorbed hydrogen, which drastically decreases the surface energy of diamond, will promote the nucleation of diamond over graphite. The adsorbed hydrogen increases the "atomic roughness" of the surface; i.e., increases the number of potential nucleation sites.

Here one should note that adsorbed hydrogen plays dual roles which may seem to be contradictory but in fact are not. On the one hand, it maintains surface order and the diamond lattice structure right to the very outer surface layer of carbon atoms by saturating the "dangling" bonds. On the other hand, by drastically lowering the surface energy of diamond, it permits a larger number of surface vacancies and adatoms to exist in equilibrium. These defects, although small in absolute number, are important in acting as nucleation sites for crystal growth. Detailed calculations of the amount of hydrogen coverage, surface energies, and surface roughness are given by Stanko [19] of our laboratory. They are not reproduced here.

B. Maximum Estimated Growth Rates

We next will estimate maximum possible growth rates by extrapolation of our experimental observations. Our experiments indicate maximum initial growth rates of 13%/hour at 1438°K on diamond powder of nominal size range 0-1 μ. This material has a specific surface area on the order of 10 square meters per gram. For purposes of computation we assume that growth takes place at a uniform rate over the surface. With this simplifying assumption the appropriate rate expression is

$$\frac{dM}{dt} = kA \tag{1}$$

where k is the rate constant, A the total area and M the total mass of the sample. Setting A = Ma, where a is the specific surface area, we find

$$\frac{1}{M}\frac{dM}{dt} = ka \tag{2}$$

For simplicity we assume the seed crystals are identical spheres. One can easily show that a=3/rρ where r is the seed radius and ρ the density of diamond. Therefore, one obtains

$$\frac{1}{M}\frac{dM}{dt} = \frac{3k}{\rho}\frac{1}{r} \tag{3}$$

Equation (3) may be rewritten in terms of the radius of an individual seed crystal. Setting $M = N\rho(\frac{4}{3}\pi r^3)$, where N is the number of seed crystals, we immediately find

$$\frac{dr}{dt} = \frac{k}{\rho} \tag{4}$$

The above simple expressions may be used to compute the rate constant, k , from our experimental observations.

For ease of computation and to be somewhat conservative, we will assume that at a temperature of 1500°K and a methane pressure of .41 Torr, we have a growth rate of 10 percent per hour; i.e., $\frac{1}{M}\frac{dM}{dt} = 0.1$ hour^{-1}. Setting $a = 10$ m^2/g, we find $k = 10^{-6}$ g/cm^2 hour. The linear growth rate, k/ρ , is thus 2.85×10^{-7} cm/hour or 6.85×10^{-2} µ/day.

The rate constant k , appears to have an Arrhenius type temperature dependence

$$k = k_o\, e^{-E/RT} \tag{5}$$

Setting E equal to our observed value of 55 Kcal, we find from Equation (5) a linear growth rate, $k/\rho \cong 1.44$ µ/day at 1800°K. The maximum possible temperature that one could use without graphitizing the diamond is probably on the order of 2000°K. At this temperature we estimate a linear growth rate of 6.71 µ/day. If we use the value of activation energy of 80 Kcal reported by the Soviet workers [9], we predict even higher linear growth rates, i.e., 6 µ/day at 1800°K and 56 µ/day at 2000°K.

In the above calculations we have assumed that the methane partial pressure is held constant at .41 Torr. We can get additional increases in rate by increasing the methane pressure since the rate appears to be about first order in methane partial pressure. One is, of course, limited in this direction by the spontaneous nucleation of graphite from the gas phase at high carbon super-saturations. It is our experience that very high carbon supersaturations can be maintained in methane or methane-hydrogen mixtures in an extremely clean vacuum system with no nuclation of graphite whatsoever. For example, no graphite nucleation is observed at 20 Torr methane and 1470°K. The nucleation of graphite appears very sensitive to impurities, especially oxygen. As our vacuum techniques have improved, we have consistently been able to maintain greater carbon super-saturations without graphite nucleation. The addition of hydrogen also suppresses nucleation of graphite from the gas phase. We do not know whether this is caused simply by a lowering of the equilibrium oxygen concentration, a decrease in the gas phase carbon chemical potential, or whether a more complex phenomenon is operating. Extrapolations from our present data indicate it may be possible to completely suppress graphite nucleation even at substantial diamond growth rates.

All of the growth rates extrapolated from our experimental data lay well within the absolute upper limit we predicted earlier [17] from considerations of surface diffusion. The extrapolated growth rates, if obtainable, are exceedingly attractive from a practical point of view. It appears it may be possible to upgrade diamond dust in the 1 μ range into useful (> 20 μ) abrasive powder in a batch reaction lasting only several hours to a week. If one took one gram (5 carats) of 1 μ powder, which is essentially worthless, and upgraded it to 20 μ , one would have 40,000 carats of diamond worth approximately $60,000.

The economics of the process obviously depend critically on the actual rates obtainable. In practice, several other factors may limit the growth rates. If it is necessary to cycle growth and cleaning operations, the net diamond growth rate will be reduced by perhaps a factor of two. At the very highest temperatures gas phase diffusion through the powder may limit the rates. Deryagin [9] has, in fact, reported this. Also, it may be necessary to reduce the methane partial pressure at the highest temperatures in order to avoid homogeneous nucleation of graphite in the gas phase.

VI. PERSONNEL

The research is conducted jointly by Professors Nelson C. Gardner and John C. Angus. Professor Gardner is a physical chemist whose specialty is surface chemistry. Professor Angus, of the Engineering School, has worked on low pressure diamond growth since 1961. Three graduate students are currently associated with this work--Mr. Satya Chauhan, Mr. Clifford Smith and Mr. John Forgac. Dr. David J. Poferl was responsible for the work on boron doped diamond and Mr. Thomas Dyble for the VLS studies. Dr. Pei Sung worked on various aspects of direct and metal catalyzed growth. The latter three workers completed their work and are no longer associated with the project.

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APPENDIX

GROWTH OF DIAMOND AND SEMICONDUCTING DIAMOND

AT SUBATMOSPHERIC PRESSURES

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INTRODUCTION

Diamond growth at low pressures, outside the field of thermodynamic stability, has been achieved by several workers (1,2,3). In this paper we present further evidence confirming that diamond can indeed be grown under conditions where it is metastable with respect to graphite and also report the growth of p-type semiconducting diamond from the vapor.

GROWTH OF SEMICONDUCTING DIAMOND FROM THE VAPOR

The production of p-type semiconducting diamond by vapor phase deposition from a methane-diborane gas mixture on natural type diamond seed crystals has been achieved. Depositions took place at 1050°C and 0.2 Torr using a gas

composition of 0.83 volume percent diborane in methane. The apparatus and analytical techniques have been described earlier (2). The seed crystals were 1 micron nominal size, natural, Type I diamonds.

Evidence confirming the growth of boron doped diamond included chemical etching, x-ray and electron diffraction, density measurements, Seebeck and resistivity measurements, chemical analysis, optical absorption induced electron emission spectroscopy, scanning electron microscopy, and electron spin resonance experiments. Blank runs using hydrogen-diborane mixtures showed no weight gains, doping, or evidence of the formation of boron carbide. Optical absorption measurements indicate the absorption edge of the new growth has been shifted toward longer wavelengths. A striking feature of the boron doped crystals was their blue color, which increased in intensity during subsequent doping runs. The epitaxial layers may contain a large number of defects. Since the added layers are very thin, their properties may reflect the close proximity of the surface.

Cumulative weight increases during the boron doping experiments were as high as 9.86 percent after six doping runs. Results of chemical analysis indicate that the concentration of boron in the diamond sample after a 9.86 percent cumulative weight increase was between 100 and 1010 ppm depending on whether the increase in boron content during doping was considered uniformly distributed through the seed crystals or limited solely to the region of new diamond growth. The relative Seebeck coefficient for the boron doped diamond was approximately 296μV/°C after a 4.57 percent weight gain and 120μV/°C after a cumulative weight increase of 9.86 percent. The sign of the Seebeck voltage after doping was indicative of a p-type semiconductor.

Details of all of the identification procedures are given by Poferl (4).

An unusual feature of the boron doping experiments was the high initial rates followed by a marked decrease in new diamond growth with each successive run on the sample. The boron apparently initially acts as a catalyst. A similar effect, but less pronounced, was noticed on runs using pure methane.

GROWTH OF UNDOPED DIAMOND IN MICROBALANCE

In situ measurements of the instantaneous growth rates of diamond powder from pure methane at low pressures were made in a high vacuum microbalance. Temperatures were from 900 to 1050°C and pressures from 9×10^{-4} Torr to 0.1 Torr. The initial growth rates were as high as 15% per hour, but decreased to about 2 percent per hour after several hours of continuous growth. The data is consistent with a growth mechanism involving the filling of active surface sites such as edges and kinks. This conclusion is supported by theoretical calculations that indicate that diamond surfaces in equilibrium with carbon or hydrocarbon vapors are probably atomically smooth. Another possible explanation for the decrease in growth rates is poisoning of the surface by small amounts of silicon or decreased mass transfer rates caused by particle sintering.

Etching of 0 to 1 micron diamond powders was performed using atomic hydrogen as the etchant. The powders sintered together into agglomerates several microns in diameter even in the absence of methane. The etching was done in the range from 10^{-2} to 10^{-1} Torr and 700 to 800°C using atomic hydrogen produced by a hot tungsten filament. Electron microprobe analysis indicated no silicon, iron, tungsten or aluminum was present.

1. William G. Eversole, Canadian Patent 628,567, Oct. 3, 1961;
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2. John C. Angus, Herbert A. Will and Wayne S. Stanko,
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3. B. V. Deryagin, D. V. Fedoseev et al. Dokl. Akad. Nauk SSSR,
   181(5) 1090 (1968) [Sov. Phys. Dokl. 13, 779 (1969)]. This is
   the first of an extensive series of papers by Deryagin and
   co-workers on the growth of diamond whiskers.

4. David J. Poferl, "Growth of Boron Doped Diamond by Vapor
   Deposition," Ph.D. Thesis, Case Western Reserve University,
   Cleveland, Ohio (1971). Available from University Microfilms,
   Ann Arbor, Mich.